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# REACTIONS OF HEXAFLUOROTHIOACETONE DIMER WITH ALCOHOLS IN THE PRESENCE OF FLUORIDE ION

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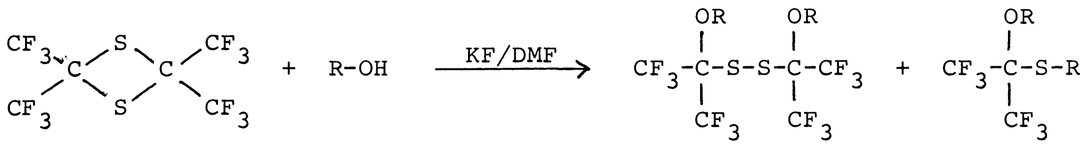
Hexafluorothioacetone dimer [1] in KF/DMF system reacted with alcohols to give disulfides 2 and alkylthio compounds 3. The reaction mechanism was speculated.

In earlier communication1), we have reported that 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithiethane [1], hexafluorothioacetone dimer, reacted with arylamines or carbonyl reagents in dimethylformamide, affording N-substituted hexafluoroisopropylidenimines. However, it was unsuccessful to have other nucleophiles such as alcohols react with 1.

In our continued studies on the nucleophilic reactions on 1, we have found that in the presence of potassium fluoride, the dimer [1] in dimethylformamide reacted with alcohols, and bis(2,2,2-trifluoro-1-alkoxy-1-trifluoromethylethyl) disulfides [2] and 2,2,2-trifluoro-1-alkoxy-1-trifluoromethylethyl alkyl sulfides[3] were obtained.



1 2 3

For example, into a mixture of potassium fluoride (4.6 g, 0.08 mol), 1 (14.6 g, 0.04 mol) and dimethylformamide (30 ml), methyl alcohol (3.8 g, 0.12 mol) was added dropwise, and the whole was stirred for 24 hr at room temperature. The reaction mixture was poured into water, and the separated oily matter was extracted with ethyl ether. The extract was dried over magnesium sulfate and the solvent was evaporated. Vacuum distillation of the residue gave 3 [R=Me], bp 101-102°C/120 mmHg (3.8 g, 23 %, Found : F, 50.3 %, Calcd : F, 50.0 %) and 2 [R=Me], bp 113-115°C/24 mmHg (5.8 g, 68 %, Found : F, 51.9 %, Calcd : F, 52.1 %).

The structures of these compounds were confirmed by $^{1}H$ and $^{19}F$ nmr and mass spectra. The $^{19}F$ nmr spectra of both compounds showed only one singlet signal each, e.i., -9.20 ppm for 2 and -7.20 ppm for 3 from ext. $CF_3CO_2H$ in $CCl_4$. The patterns of $^{1}H$ nmr spectra were also simple. Only one singlet signal at $\tau$ 6.28 (OMe) for 2 and two singlet signals at $\tau$ 6.40 (OMe) and 7.80 (SMe) for 3 appeared. In the mass spectrum of 2, the base peak, m/e 181 ($C_4H_3F_6O$) and other fragment peaks such as m/e 213 ($C_4H_3F_6OS$), 69 ($CF_3$), 64 ($S_2$) and 31 (OMe) appeared appropriately. The parent peak, $M^+$ 426, was not recognized, but this is not strange because in di-tert-alkyl disulfides it is known that the parent peak appears very weakly[2). The measurement of the mass spectrum was unsuccessful for 3 because of its high volatility.

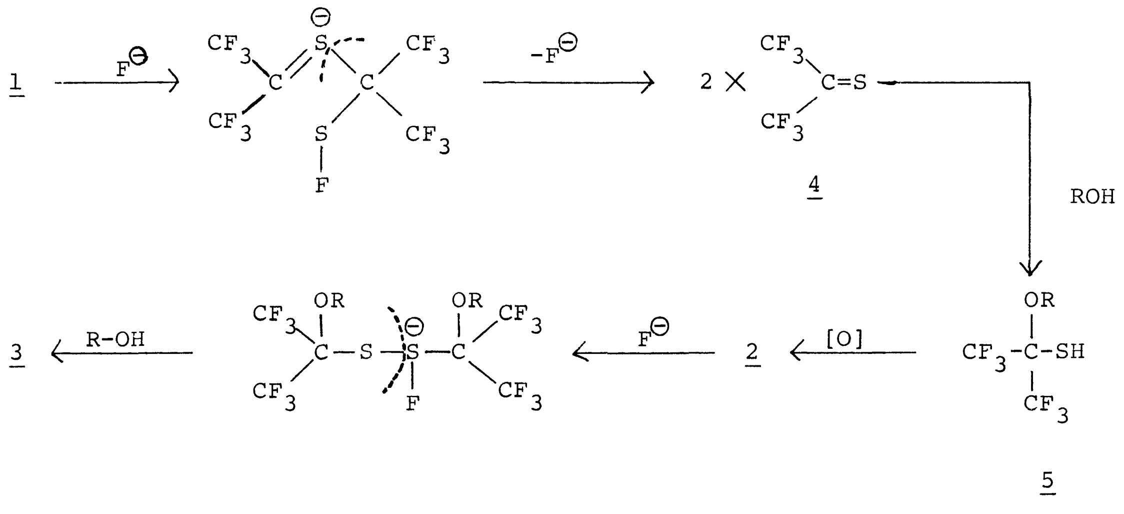
The reactions with other alcohols were run similarly, and two products, 2 and 3, were obtained in every case. The results were given in Table 1 with their $^{19}F$ nmr spectral data.

Table 1 Physical properties of 2 and 3

| R | 2 | | | 3 | | |
|---|---|---|---|---|---|---|
| | Yield (%) | Bp (°C/mmHg) | $^{19}F$ nmr ($\delta$ ppm)$^{a)}$ | Yield (%) | Bp (°C/mmHg) | $^{19}F$ nmr ($\delta$ ppm)$^{a)}$ |
| Me | 68 | 113-115/24 | -9.20 | 23 | 101-102/120 | -7.20 |
| Et | 69 | 131-132/43 | -8.40 | 27 | 125-126/43 | -8.00 |
| n-Pr | 77 | 132-134/24 | -8.20 | 23 | 118-120/24 | -7.40 |
| i-Pr | 46 | 138-140/20 | -8.40 | 15 | 128-131/20 | -7.35 |
| n-Bu | 66 | 155-156/23 | -8.80 | 21 | 148-149/24 | -7.65 |
| i-Amyl | 51 | 159-160/23 | -8.62 | 33 | 131-134/23 | -7.90 |

a) From ext. $CF_3CO_2H$ in $CCl_4$.

Although further investigation is necessary in order to elucidate the mechanism, it appears that the reaction was initiated by the active fluoride ion in the polar aprotic solvent which attacked sulfur atom of the dimer 1, and it accelerated the formation of reactive hexafluorothioacetone monomer 4. Alcohol as a nucleophile reacted with 4, giving 2,2,2-trifluoro-1-alkoxy-1-trifluoromethylethanethiol [5], which was oxidized to disulfide 2. Attack of fluoride ion on sulfur occurred again, and the resulted sulfur anion must have reacted with alcohol to give 3.



## References

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2) D. H. Williams, J. H. Bowie, S. O. Lawesson, J. Ø. Madsen, C.Nolde,and G. Schroll, J. Chem. Soc. (B), 1966, 946.

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